OMB No. 0925-0001 and 0925-0002 (Rev. 03/2020 Approved Through 02/28/2023)

BIOGRAPHICAL SKETCH

Provide the following information for the Senior/key personnel and other significant contributors.
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NAME: Decato, Daniel A.

eRA COMMONS USER NAME (credential, e.g., agency login): DDECATO

POSITION TITLE: Small Molecule X-ray Diffraction and NMR Core Manager

EDUCATION/TRAINING (Begin with baccalaureate or other initial professional education, such as nursing, include postdoctoral training and residency training if applicable. Add/delete rows as necessary.)

| INSTITUTION AND LOCATION | DEGREE(if applicable) | Completion DateMM/YYYY | FIELD OF STUDY |
| --- | --- | --- | --- |
| University of Wisconsin-Eau Claire | B.S. | 05/2013 | Chemistry |
| University of Montana | Ph.D. | 09/2020 | Supramolecular Chemistry |

**A. Personal Statement
My passion for collaborative scientific efforts became evident during my undergraduate work operating a transmission electron microscope to image silver nanoparticles. I have since been able to continue this calling by managing the small molecule X-ray diffraction facility at the University of Montana since its inception in 2014. Having no prior background in crystallography, I took the initiative to teach myself and pursue various crystallographic workshops under the guidance of Professor Orion Berryman. I quickly advanced my skillset and fully embraced the collaborative nature of crystallography—contributing significantly to the facility’s ascension to a regional resource, servicing investigators in Montana, Washington, Idaho, and Utah. Now as a skilled young crystallographer (well over 300 structures solved), I realize my humble crystallographic beginnings make me uniquely positioned to disseminate crystallography to diverse groups of scientists; I understand the steep learning curve to X-ray crystallography. To lessen this barrier, I have i**ndependently conducted seminars about small molecule **X-ray** crystallography (e.g. theory, crystal growing, data handling, impacts on research efforts) to faculty and students at the University of Montana. These efforts also highlight my ongoing commitment to collaborative science. M**y** long-term career goals are to manage a small molecule X-ray diffraction facility while maintaining a small research program centered on crystal engineering studies. With an eye toward the future, I maintain a desire to add to my current skillset and branch into macromolecular crystallography as well as the CryoEM technique of microcrystal electron diffraction MicroED.

**B. Positions and Honors**

**Positions and Employment**

2013-2014 Laboratory Teaching Assistant, University of Montana, Missoula MT

2014- 2020 Research Assistant, Dr. Orion Berryman, University of Montana, Missoula MT

2014- Small Molecule X-ray Diffraction Core Manager, University of Montana, Missoula MT

2020- NMR Core Manager, University of Montana, Missoula MT

**Other Experience and Professional Memberships**

2013- Member, American Crystallographic Association

2018 Faculty Evaluation Committee University of Montana

2019-2020 Chair Elect, Young Scientists Scientific Interest Group, American Crystallographic Association

2019- Reviewer- Acta Crystallographica Section C, Dalton Transactions, Scientific Reviews, Crystal Growth and Design

2020- Member of Nomination Committee, American Crystallographic Association

2020- Chair, Young Scientists Scientific Interest Group, American Crystallographic Association

**Honors**

2015 American Crystallographic Association Travel Grant (ACA Summer School)

2016 Stanley R. Ames Scholarship

2018 Bertha Morton Fellowship

2018 Besancon Scholarship

2019 American Crystallographic Association Travel Grant (ACA Annual Meeting)

2019 Crystals (Multidisciplinary Digital Publishing Institute) Travel Award

2019 Clarkson University Travel Award

**C. Contributions to Science**

**Publications and papers: 21 peer reviewed publications, 3 invited book chapters.**

1. **Supramolecular Studies Elucidating and Quantifying Nuances of the Halogen and Hydrogen Bond Relationship**

A continued expansion of halogen bonding materials coupled the ubiquitous nature of the hydrogen bond (HB) highlight the inevitable—that halogen bond (XB) donors and HB donors will interact. Understanding how these noncovalent interactions affect (and compare to) each other is of fundamental importance to both large and small molecule studies. My doctoral research largely centered on efforts to address fundamental knowledge deficiencies in this chemical space. My early graduate work contributed to comparative studies, pitting the XB against the HB, to uncover XB features relative to the HB.1 This was followed by studies evaluating the Cambridge Structural Database that brought into question the reported geometrical orthogonal relationship between the HB and XBs when simultaneously interacting with a single carbonyl oxygen.2 Since then, my focus has been on the Hydrogen Bond-enhanced Halogen Bond (HBeXB).3-5 The HBeXB is an example of noncovalent cooperativity in which a HB to the electron-rich belt of a XB donor atom further polarizes the halogen, thus producing a stronger XB. The seminal study (solution, solid-state, and theoretical) showed the that an HB to an iodine XB donor of a bidentate anion receptor engendered preorganization of molecular structure while simultaneously enhancing XB interactions with anions.3 The complexities of preorganization effects in this system complicated the physical evidence of HBeXB augmentation, motivating a follow up study.4 Here, through theoretical and experimental quantification of neutral and charge-assisted monodentate HBeXB donors, we showed that HBeXB enhancement effects are more readily realized in electron-rich systems. In terms of halogenated drug design, bioengineering, and supramolecular assemblies, this feature is advantageous. For example, strong activation of XB donors can leave XBing molecules more susceptible to dehalogenation, rendering them ineffective. Incorporating an intra- or intermolecular HB to the electron rich belt of a XB donor allows for a less reactive XB donor to be used while preserving strong XB contacts. Considering over half of all launched organohalogen drugs contain heavy halogens (X= Cl, Br, I), with the capacity for XBing, this finding has significant far-reaching potential. Substituent effects to elucidate structure−activity relationships between XBs and HBs are concluding and are to be published within the next six months.5 I served as the crystallographer on all these studies, as well as a main contributor to experimental design and manuscript preparation. In reference 3 I was also the main theoretical chemist carrying out the computations and in 4 I was the main synthetic and theoretical chemist carrying out the experiments.

1. Riel, A. M. S.; Jessop, M. J.; **Decato, D. A.**; Massena, C. J.; Nascimento, V. R.; Berryman O. B., “Experimental Evidence of Halogen Bond Hard-Soft Acid-Base Complementarity.” Acta Crystallographica Section B, 2017, B73, 203-209.
2. **Decato, D. A.**; Berryman, O. B., (2017). 12. Simultaneous Halogen and Hydrogen Bonding to Carbonyl and Thiocarbonyl Functionality. Multi-Component Crystals: Synthesis, Concepts, Function (pp. 272-288). Berlin, Boston: De Gruyter.
3. Riel, A. M. S. ‡; **Decato, D. A.** ‡; Sun, J.; Massena, C.J.; Jessop, M.J.; Berryman, O.B., “Intramolecular Hydrogen Bonded-Halogen Bond: A New Strategy for Preorganization and Enhancement.” Chemical Science. 2018, 9, 5828–5836. ‡ Co-authors (each author contributed equally).\*\*Part of themed collection: Most popular 2018-2019 supramolecular chemistry articles
4. **Decato, D. A.**; Riel, A. M. S.; May, J; Berryman, O.B., “Theoretical, Solid-State, and Solution Quantification of a Monodenate Hydrogen Bond Enhanced Halogen Bond.” Angewandte Chemie International Edition 2021, *60*, 3685.
5. **Halogen Bond Helical Anion Foldamers**

**Helices and anions frequently contribute to molecular structures executing critical life functions such as information storage, cell signaling, catalysis and specific binding. Nature achieves these feats by synthesizing amino acid polymers that fold into functional shapes (e.g. proteins, DNA, RNA). Biotic structures are limited in their building blocks; whereas the synthetic chemist is not bound by these restrictions and in theory is only limited by imagination. As such, we have turned to the XB—**a noncovalent interaction between an electrophilic halogen and a Lewis base—for the construction of helical anion foldamers targeted for eventual use as therapeutics. The XB has received enormous attention from diverse chemical fields, in part for its strict linear geometry compared to the hydrogen bond. This linearity, driven by the anisotropic distribution of electron density that develops on an electron-deficient halogen, we have found engenders the formation of multi-strand anion helicates.1 We have utilized this system to further elucidate the kinetics of anion (guest) exchange as well as ligand (strand) exchange.2 Two related projects have grown from these findings. First is the construction of a family of oligomers up to 15 repeat units with systematically varied substituents for fundamental anion transport studies. The second is a single strand anion foldamer has been developed to elucidate and quantify π-π stacking. While many computational evaluations have evaluated π-stacking, few experimental studies have quantified electronic ring effects on foldamers and molecular preorganization. Specifically, a seven-ring arylethynyl oligomer results in only the terminal rings overlapping (theoretical analysis) in a face-to-face stacked manner. I served as the crystallographer on all these studies and contributed to manuscript preparation and editing. The forthcoming single strand foldamers study I am the main synthetic and theoretical chemist carrying out most of the experiments and manuscript preparation.

1. Massena, C. J.; Wageling, N. B.; **Decato, D. A.**; Martin Rodriguez, E.; Rose, A. M.; Berryman, O. B. “A Halogen-Bond-Induced Triple Helicate Encapsulates Iodide.” Angewandte Chemie International Edition, 2016, 55, 12398–12402.
2. Massena, C.J.; **Decato, D. A.**; Berryman, O.B. "A Long‐Lived Halogen‐Bonding Anion Triple Helicate Accommodates Rapid Guest Exchange." Angewandte Chemie International Edition, 2018, 57, 16109–16113.
3. **Synthetic Supramolecular Crystallography of Anions**

Anions are of topical interest as many have significant metabolic roles (e.g. halides in ion channels) and/or are common targets of waste remediation. Crystallographic studies provide a snapshot into potential binding modes of receptors and synthetic anion channels. Additionally, the construction of multi-component solids (cocrystals and/or salts) is a growing interest in pharmaceuticals as these solids often have different physical properties (e.g. solubility, stability, bioavailability) than the pure mono-component material. While significant progress has been made to engineer multi-component solids, the role of anions in crystal engineering is lagging. Considering many medicines are sold as a hydrochloric salt, pursuit of solid-state guidelines that consider the impact of anions in the final assembly of crystalline materials is important. To this end, we have begun to evaluate the interplay between the protonation and/or alkylation of pyridine nitrogen atoms, steric hindrance of HBing sites, the shape of the organocation, and the identity of the anion on crystalline packing. Our initial studies involving the perrhenate anion, a tractable surrogate for the medically relevant pertechnetate, highlighted the differing role of alkylation and protonation.1 In another study, we evaluated the influence of increasing steric hindrance at the urea HBing site of pyridinium urea organocatalysts had on both solid-state packing and solution phase catalysis. Lastly, in our most recent study, we began to consider effects of packing as being dictated by the larger organocation rather than dictated by the anion. This perception change, moving focus from the anion to the cation, was realized during our evaluation of a large number of cationic arylethynyl structures.3 We found that while anions support the solid-state formation of dimers, the molecular geometry and characteristics (planarity, rigidity, and directionality) of arylethynyl systems increase the likelihood of dimer formation by limiting efficient packing arrangements. Collectively these studies represent the first steps towards developing guidelines for anion incorporation within established crystal engineering strategies. I served as the crystallographer on all these studies and contributed significantly to manuscript preparation and editing.

1. Riel, A. M. S.; **Decato, D. A.**; Berryman, O.B., “Protonation and Alkylation Induced Multidentate C-H Anion Binding to Perrhenate.” Crystal Growth Design, 2016, 16, 974–980.
2. Wageling, N. B.; **Decato, D. A.**; Berryman, O. B. "Steric Effects of pH Switchable, Substituted (2-pyridinium)urea Organocatalysts: a Solution and Solid Phase Study." Supramolecular Chemistry, 2018, 30, 1004–1010.
3. **Decato, D. A.**; Riel, A. M. S.; and Berryman, O.B., “Structural Analysis of 1,3-bis(4-ethynyl-3-iodopyridinium)-benzene Halogen Bond Donors” Crystals, **2019**, 9, 522.

**D. Research Support**

Current

NIH 1 P20 GM103546 (Sprang, PD) 08/1/2016 – 07/31/2021

Center for Biomolecular Structure and Dynamics

The goal of this project is to support a Center of excellence in Biomolecular Structure and Dynamics to conduct research to understand the biophysical basis of human disease. The Integrated Structural Biology Core supports the research of center investigators who need structural studies of small molecules by X-ray crystallography. The core also supports investigators who need to conduct NMR studies of small molecule and macromolecular species.

Role: Core manager for small molecule X-ray diffraction and NMR.